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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: REDUCTION OF METAL OXIDES IN AN ELECTROLYTIC CELL

(57) Abstract: A method of reducing a titanium oxide in a solid state in an electrolytic cell which includes an anode, a cathode formed at least in part from the titanium oxide, and a molten electrolyte which includes cations of a metal that is capable of chemically reducing the cathode titanium oxide, wch method includes operating the cell at a potential that is above a potential at which cations of the metal that is capable of chemically reducing the cathode titanium oxide deposit as the metal on the cathod, whereby the metal chemically reduces the cathode titanium oxide, and which method is characterised by refreshing the electrolyte and/or changing the cell potential in later stages of the operation of the cell as required having regard to the reactions occurring in the cell and the concentration of oxygen in the titanium oxide in the cell in order to produce high purity titanium.



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REDUCTION OF METAL OXIDES IN AN ELECTROLYTIC CELL

The present invention relates to reduction of metal oxides in an electrolytic cell.

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The present invention was made during the course of an on-going research project on the electrolytic reduction of titania (TiO_2) carried out by the applicant.

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During the course of the research project the applicant carried out experimental work on an electrolytic cell that included a graphite crucible that formed an anode of the cell, a pool of molten CaCl_2 -based electrolyte in the crucible, and a cathode that included solid

15

titania.

One objective of the experimental work was to reproduce the results reported in International application PCT/GB99/01781 (Publication no. WO99/64638) in the name of Cambridge University Technical Services Limited and in technical papers published by the inventors.

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The Cambridge International application discloses two potential applications of a "discovery" in the field of metallurgical electrochemistry.

25

One application is the direct production of a metal from a metal oxide.

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In the context of this application, the "discovery" is the realisation that an electrolytic cell can be used to ionise oxygen contained in a metal oxide so that the oxygen dissolves in an electrolyte. The Cambridge International application discloses that when a suitable potential is applied to an electrolytic cell with a metal oxide as a cathode, a reaction occurs whereby

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oxygen is ionised and is subsequently able to dissolve in the electrolyte of the cell.

European patent application 9995507.1 derived
5 from the Cambridge International application has been allowed by the European Patent Office.

The allowed claims of the European patent application *inter alia* define a method of electrolytically
10 reducing a metal oxide (such as titania) that includes operating an electrolytic cell at a potential that is lower than the deposition potential of cations in the electrolyte.

15 The Cambridge European patent application does not define what is meant by deposition potential and does not include any specific examples that provide values of the deposition potential for particular cations.

20 However, submissions dated 2 October 2001 to the European Patent Office by the Cambridge patent attorneys, which pre-dated the lodgement of the claims that were ultimately allowed, indicate that they believe that the decomposition potential of an electrolyte is the
25 deposition potential of a cation in the electrolyte.

Specifically, page 5 of the submissions state that:

30 "The second advantage described above is achieved in part through carrying out the claimed invention below the decomposition potential of the electrolyte. If higher potentials are used then, as noted in D1 and D2, the cation in the electrolyte deposits on the metal or semi-
35 metal compound. In the example of D1, this leads to calcium deposition and therefore consumption of this reactive metal.....During operation of the method, the

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electrolytic cation is not deposited on the cathode".

Contrary to the findings of Cambridge, the experimental work carried out by the applicant has established that it is essential that the electrolytic cell be operated at a potential that is above the potential at which Ca^{++} cations in the electrolyte can deposit as Ca metal on the cathode.

Specifically, as a consequence of the experimental work, the applicant has invented a method of reducing a metal oxide such as titanium oxides in a solid state in an electrolytic cell which includes an anode, a cathode formed at least in part from the metal oxide, and a molten electrolyte which includes cations of a metal that is capable of chemically reducing the cathode metal oxide, which method includes a step of operating the cell at a potential that is above a potential at which cations of the metal that is capable of chemically reducing the cathode metal oxide deposit as the metal on the cathode, whereby the metal chemically reduces the cathode metal oxide.

The above method is described in Australian provisional application PS3049 in the name of the applicant lodged on 20 June 2002, and the disclosure in the patent specification lodged with the application is incorporated herein by cross-reference.

In addition to the above, the experimental work (and associated theoretical analysis work) carried out by the applicant has determined a number of important factors that play a role in the actual reduction process.

The relevant experimental data indicates that (i) Cl_2 gas is removed at the anode of the electrolytic cell at potentials well below the theoretical decomposition

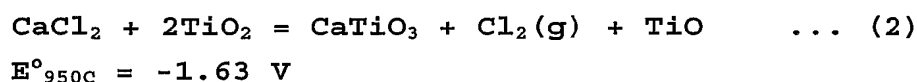
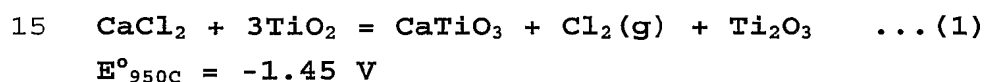
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potential of the electrolyte CaCl_2 , (ii) $\text{Ca}_x\text{Ti}_y\text{O}_z$, is present at the cathode during some stages of the electrolysis, and (iii) CaO is formed in the molten electrolyte bath.

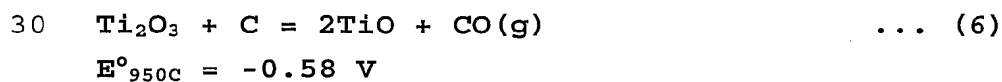
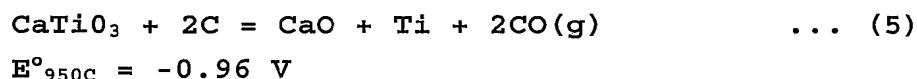
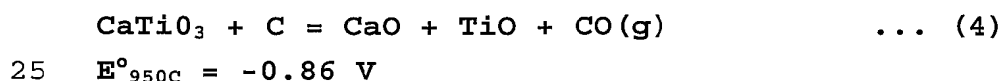
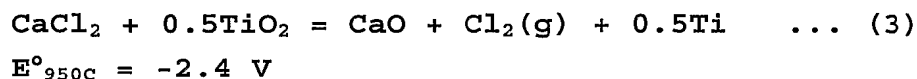
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In view of the above, the applicant has concluded that a number of steps are involved in the method of reducing titanium oxides and that some of these steps are represented by reactions (1) to (8) mentioned below.

10 Reactions (1) to (8) relate to reduction of titanium oxides using an electrolytic cell with CaCl_2 (containing O^- anions) as the electrolyte and a graphite anode, with their standard potentials at 950°C .



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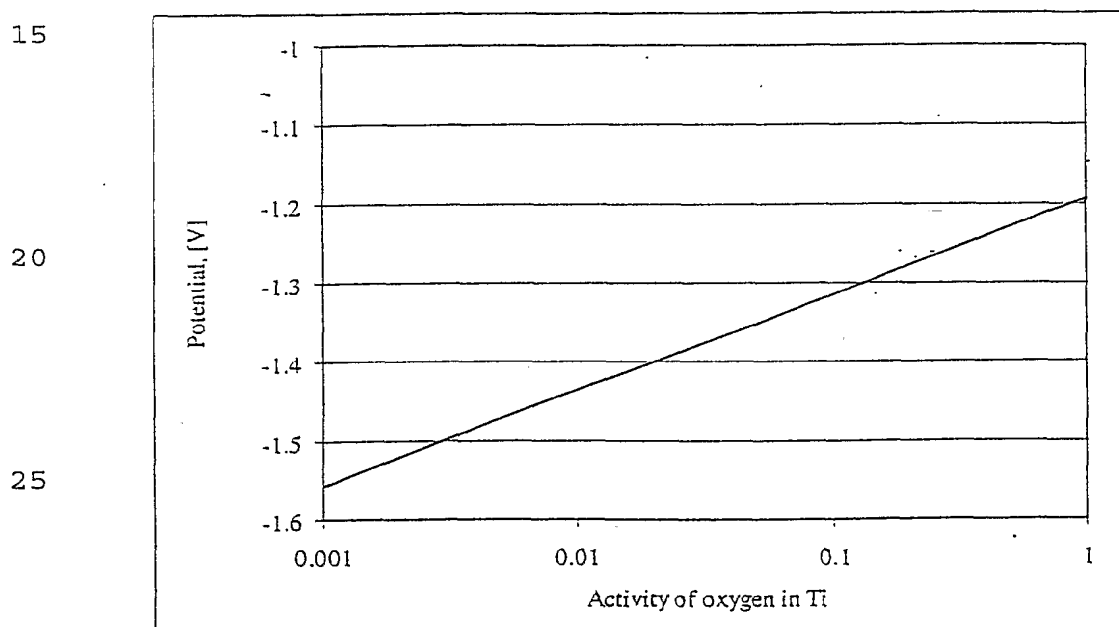
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Reactions (1) to (8) are not an exhaustive list, of the possible reaction and other reactions can take place. Specifically, the applicant suspects that other reactions, involving titanium suboxides, represented by the formula Ti_nO_{2n-1} , and calcium titanates, represented by the formula $CaTi_nO_{3n+1}$, can take place.

The potential of reaction (8) in particular varies with the concentration of oxygen in titanium. The following graph illustrates the variation of potential with concentration of oxygen in titanium in a cell operating at 950°C. The graph was prepared by the applicant using published data.



It is clear from the graph that reaction (8) requires higher potentials at lower concentrations of oxygen and thus there is increased resistance to oxygen removal as the oxygen concentration decreases.

The solubility of different titanium oxides in $CaCl_2$ is not taken into consideration in the calculation of the potentials for reactions (1) to (8). The significance

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of this is that some of reactions (1) to (8) may take place at potentials that are higher or lower than the potentials stated above at the stated temperature of 950°C.

5 For example, reduced activity of TiO will reduce the value of the potentials of reactions (2), (4) and (6) (i.e. make the potentials more positive) and at the same time will increase the potential of reaction (7) (i.e. make it more negative).

10

 In view of the above, the applicant has realised that it is likely to be extremely difficult to reduce titanium oxide in an electrolytic cell to titanium (α Ti) of high purity, i.e. low concentration of oxygen (no more
15 than 100ppm oxygen) in a single stage operation.

 Specifically, the applicant has realised that it is necessary to refresh the electrolyte and/or to change cell potential in a later stage or in later stages of the
20 operation of the electrolytic cell in order to reduce titanium oxide in an electrolytic cell to α titanium of high purity, ie low concentration of oxygen.

 According to the present invention there is
25 provided a method of reducing a titanium oxide in a solid state in an electrolytic cell which includes an anode, a cathode formed at least in part from the titanium oxide, and a molten electrolyte which includes cations of a metal that is capable of chemically reducing the cathode
30 titanium oxide, which method includes operating the cell at a potential that is above a potential at which cations of the metal that is capable of chemically reducing the cathode titanium oxide deposit as the metal on the cathode, whereby the metal chemically reduces the cathode
35 titanium oxide, and which method is characterised by refreshing the electrolyte and/or changing the cell potential in later stages of the operation of the cell as

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required having regard to the reactions occurring in the cell and the concentration of oxygen in the titanium oxides in the cell in order to produce high purity titanium (α Ti).

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The term "high purity" is understood to mean that the concentration of oxygen is no more than 100ppm in the titanium.

10 In effect, the present invention is concerned with selecting the operating conditions of the cell, including cell potential and/or electrolyte composition, during various stages of the operation in the cell having regard to the reactions that take place in the cell. The applicant envisages at this stage that commercial
15 operations will be at constant current and that it may not be possible to achieve voltages required to remove oxygen to very low levels because of composition changes in the electrolyte. In these circumstances, refreshing and or changing the electrolyte composition is important in order
20 to produce a high purity α titanium.

The above-described method makes it possible to produce titanium of high purity with respect to oxygen in an electrolytic cell and without refining or otherwise
25 processing the titanium outside the electrolytic cell.

The method may include refreshing the electrolyte by adding new electrolyte to the existing electrolyte or otherwise adjusting the composition of the electrolyte.
30

In addition, the method may include carrying out the method in a series of electrolytic cell and successively transferring the partially reduced titanium oxide to each of the cells in the series.
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The composition of the electrolyte in each cell may be selected having regard to the reactions occurring

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in the cell and the concentration of oxygen in the titanium oxide in the cell.

5 The cell potential may be changed at different stages in the method on a continuous or a step-change basis.

10 Preferably the metal deposited on the cathode is soluble in the electrolyte and can dissolve in the electrolyte and thereby migrate to the vicinity of the cathode titanium oxide.

15 It is preferred that the electrolyte be a CaCl_2 -based electrolyte that includes CaO as one of the constituents of the electrolyte.

20 In such a situation it is preferred that the cell potential be above the potential at which Ca metal can deposit on the cathode, i.e. the decomposition potential of CaO .

25 The decomposition potential of CaO can vary over a considerable range depending on factors such as the composition of the anode, the electrolyte temperature and electrolyte composition.

30 In a cell containing CaO saturated CaCl_2 at 1373K (1100°C) and a graphite anode this would require a minimum cell potential of 1.34V.

It is also preferred that the cell potential be below the decomposition potential of CaCl_2 .

35 In a cell containing CaO saturated CaCl_2 at 1373K (1100°C) and a graphite anode this would require that the cell potential be less than 3.5V.

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The decomposition potential of CaCl_2 can vary over a considerable range depending on factors such as the composition of the anode, the electrolyte temperature and electrolyte composition.

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For example, a salt containing 80% CaCl_2 and 20% KCl at a temperature of 900K (657°C), decomposes to Ca (metal) and Cl_2 (gas) above 3.4V and a salt containing 100% CaCl_2 at 1373K (1100°C) decomposes at 3.0V.

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In general terms, in a cell containing CaO-CaCl_2 salt (not saturated) at a temperature in the range of 600-1100°C and a graphite anode it is preferred that the cell potential be between 1.3 and 3.5V.

15

The CaCl_2 -based electrolyte may be a commercially available source of CaCl_2 , such as calcium chloride dihydrate, that partially decomposes on heating and produces CaO or otherwise includes CaO .

20

Alternatively, or in addition, the CaCl_2 -based electrolyte may include CaCl_2 and CaO that are added separately or pre-mixed to form the electrolyte.

25

It is preferred that the anode be graphite or an inert anode.

The cell may be of the type disclosed in the drawings of the patent specification lodged with Australian provisional application PS3049.

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CLAIMS

1. A method of reducing a titanium oxide in a solid state in an electrolytic cell which includes an anode, a cathode formed at least in part from the titanium oxide, and a molten electrolyte which includes cations of a metal that is capable of chemically reducing the cathode titanium oxide, which method includes operating the cell at a potential that is above a potential at which cations of the metal that is capable of chemically reducing the cathode titanium oxide deposit as the metal on the cathode, whereby the metal chemically reduces the cathode titanium oxide, and which method is characterised by refreshing the electrolyte and/or changing the cell potential in later stages of the operation of the cell as required having regard to the reactions occurring in the cell and the concentration of oxygen in the titanium oxides in the cell in order to produce high purity titanium (α Ti).
2. The method defined in claim 1 wherein the metal deposited on the cathode is soluble in the electrolyte and can dissolve in the electrolyte and thereby migrate to the vicinity of the cathode titanium oxide.
3. The method defined in claim 1 or claim 2 wherein the electrolyte is a CaCl_2 -based electrolyte that includes CaO as one of the constituents of the electrolyte.
4. The method defined in claim 3 wherein the cell potential be above the potential at which Ca metal can deposit on the cathode, i.e. the decomposition potential of CaO .
5. The method defined in claim 3 or claim 4 wherein the cell potential is below the decomposition potential of CaCl_2 .

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6. The method defined in any one of claims 3 to 5 wherein at a temperature in the range of 600-1100°C and a graphite anode the cell potential is between 1.3 and 3.5V.

5

7. The method defined in any one of claims 3 to 6 wherein the CaCl_2 -based electrolyte is a commercially available source of CaCl_2 , such as calcium chloride dihydrate, that partially decomposes on heating and produces CaO or otherwise includes CaO .

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8. The method defined in any one of claims 3 to 7 wherein the CaCl_2 -based electrolyte includes CaCl_2 and CaO that are added separately or pre-mixed to form the electrolyte.

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9. The method defined in any one of the preceding claims wherein the anode is graphite or an inert anode.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU02/00843

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| A. CLASSIFICATION OF SUBJECT MATTER | | |
| Int. Cl. ⁷ : C25C 3/28, C22B 34/12 | | |
| According to International Patent Classification (IPC) or to both national classification and IPC | | |
| B. FIELDS SEARCHED | | |
| Minimum documentation searched (classification system followed by classification symbols) IPC: C25C 3/28, C22B 34/12 | | |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched | | |
| Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DWPI: ELECTROLYT+ | | |
| C. DOCUMENTS CONSIDERED TO BE RELEVANT | | |
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A | WO 99/64638 A (CAMBRIDGE UNIVERSITY TECHNICAL SERVICES LTD) 16 December 1999 whole document | 1-9 |
| A | GB 2359564 A (THE SECRETARY OF STATE FOR DEFENCE) 29 August 2001 whole document | 1-9 |
| A | WO 01/62994 A (THE SECRETARY OF STATE FOR DEFENCE) 30 August 2001 whole document | 1-9 |
| <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex | | |
| <p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> | | |
| Date of the actual completion of the international search 27 August 2002 | | Date of mailing of the international search report 5 SEP 2002 |
| Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaaustralia.gov.au Facsimile No. (02) 6285 3929 | | Authorized officer B. PREMARATNE Telephone No : (02) 6283 2407 |

INTERNATIONAL SEARCH REPORT

International application No.

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| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|-------------------------------------------------------|------------------------------------------------------------------------------------|-----------------------|
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A | US 4518426 A (MURPHY) 21 May 1985 whole document | 1-9 |
| A | US 4381976 A (ARMAND) 3 May 1983 whole document | 1-9 |

INTERNATIONAL SEARCH REPORT

International application No.

Information on patent family members

PCT/AU02/00843

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

| Patent Document Cited in Search Report | | | | Patent Family Member | | | |
|-------------------------------------------|---------|----|-----------|----------------------|-----------|----|-----------|
| WO | 9964638 | AU | 42770/99 | BR | 9910939 | CZ | 20004476 |
| | | EP | 1088113 | HU | 200102934 | NO | 20006154 |
| | | PL | 344678 | | | | |
| GB | 2359564 | AU | 200133871 | AU | 200133876 | AU | 200133890 |
| | | WO | 200162994 | WO | 200162995 | WO | 200162996 |
| | | GB | 2362164 | | | | |
| US | 4518426 | US | 4487677 | AU | 27774/84 | CA | 1261297 |
| US | 4381976 | EP | 53566 | FR | 2494726 | JP | 57116791 |
| | | NO | 814030 | | | | |
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